Communications

Intensification of Iron Removal Rate during Oxygen Leaching through Gas-Liquid Mass-Transfer Enhancement

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The productivity of industrially important aqueous oxygen leaching processes is limited by gas-liquid mass-transfer rates of a sparingly soluble solute, usually oxygen. The low productivity of aqueous oxygen leaching processes is usually improved through operation at elevated temperatures and pressures.[1,2] However, these processes become economically viable only at large capacities due to their high capital cost. In the Becher process[3] for the manufacture of synthetic rutile, an aqueous oxygen leaching step at near neutral pH is employed to remove the metallic iron component from reduced ilmenite. However, the oxygen leaching step suffers from a serious drawback of low productivity due to limitations imposed by the sluggish mass transport rates of oxygen from the gas phase to liquid phase. In this specific case, the use of elevated pressures has been shown to be technically impossible due to low conversions brought about by the phenomenon of passivation.[4]

The present work reports an alternate strategy for the intensification of this process at ambient conditions and ensuring environmental compatibility of the process. The results are interpreted based on the theory of gas-liquid mass-transfer enhancement. The manufacture of synthetic rutile from ilmenite mineral is carried out in two major steps. First, ilmenite is reduced through carbothermal reduction at high temperature such that the iron component is converted to the metallic phase. Reduced ilmenite (RI) resulting from this step is then subjected to oxygen leaching in an electrolyte medium to remove the iron fraction through an accelerated corrosion reaction. The oxygen leaching step, alternately known as the aeration step in the Becher process, involves electrochemical dissolution of metallic iron by cathodic reduction with dissolved oxygen in a 0.1 M ammonium chloride solution followed by liquid-phase oxidation of the Fe^{2+} accompanied by hydrolysis and precipitation of ferric ions as hydrated iron oxides. The overall reaction can be represented as[5]

$$2Fe + 3O_2 + nH_2O \rightarrow 2Fe_2O_3 \cdot nH_2O \qquad [1]$$

From the reported process chemistry, the individual reactions are

(a) Electrochemical reaction:

$$2Fe \rightarrow 2Fe^{2+} + 4e^- \qquad [2a1]$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad [2a2]$$

(b) Liquid phase oxidation of Fe^{2+}:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad [2b]$$

(c) Hydrolysis:

$$2Fe^{3+} + xH_2O \rightarrow Fe_2O_3 \cdot (x-6)H_2O + 6H^+ \qquad [2c]$$

The detailed mechanism is described elsewhere.[6] The role of ammonium chloride is to act as a buffering and complexing agent.

The experiments in the present study were carried out in a mechanically agitated sparged reactor (diameter = 0.25 m) provided with a six-bladed disc turbine; the details of the experimental setup are described in the literature.[6] The ammoniacal oxygen leaching process for iron removal was carried out by sparging air through a slurry containing RI particles suspended in ammonium chloride solution of 0.1 mol/L. The ilmenite mineral $FeTiO_3$ (TiO2-60.3 pct, FeO-0.4 pct, Fe_2O_3-24.8 pct, Al_2O_3-1 pct, SiO_2-1.4 pct, CaO-0.15 pct, MgO-0.65 pct, MnO_2-0.4 pct, Cr_2O_3-0.14 pct, V_2O_5-0.26 pct, P_2O_5-0.17 pct, and ZrO_2-0.6 pct) was supplied by Indian Rare Earths Ltd., Mumbai, (Quilon grade). The RI was prepared by roasting this raw ilmenite with coal at 1050 °C. The total iron content and metallic iron content of the reduced ilmenite were determined by chemical analysis as 28.5 pct and 22 ± 1 pct, respectively. Reduced ilmenite particles in the size ranges 100 to 150, 150 to 180, and 210 to 250 μm were employed for the experimental investigations. An aqueous solution of ferrous chloride, which was employed as the enhancing agent, was prepared by dissolving electrolytic grade iron in concentrated hydrochloric acid. The concentration range of ferrous chloride in the reacting slurry was 0 to 0.25 mol/L.

Reduced ilmenite samples were drawn at regular intervals during the leaching process. The drawn samples were repeatedly washed with water to remove iron oxide particles formed by Reaction [2c]. Then they were washed with acetone and dried. Chemical analysis for determining the total iron content of the reduced ilmenite samples was carried out as described elsewhere.[7] Conversion *vs* time data for different conditions were obtained from the residual iron content of the samples. Slurry samples were drawn simultaneously with ilmenite samples for determining the ferrous ion concentration during the process. The slurry samples were filtered and the ferrous ion concentration in the clear solution was determined by chemical analysis.

The intensification of the metallic iron removal process was evaluated during the first 2 hours of the reaction where the overall rate is controlled by the gas-liquid mass-transfer step.[6] Further, the generation of the byproduct, *viz.* iron oxide, during the initial phase of 2 hours can be considered negligible to have any influence on the rate of iron removal. Figure 1 shows that the rate of iron removal increases with the concentration of ferrous chloride in the slurry and approaches saturation. Enhancement is defined as the ratio of rate iron removal in the presence of ferrous chloride to the rate of iron removal in the absence of ferrous chloride. It reaches a saturation level at a value around 1.5, as depicted in Figure 1. It is evident from Tables I and II that the enhancement in rate of iron removal is independent of weight percentage and particle size of reduced ilmenite in the slurry. The measured concentration of ferrous ions in the drawn slurry samples remained close to the initial concentrations,

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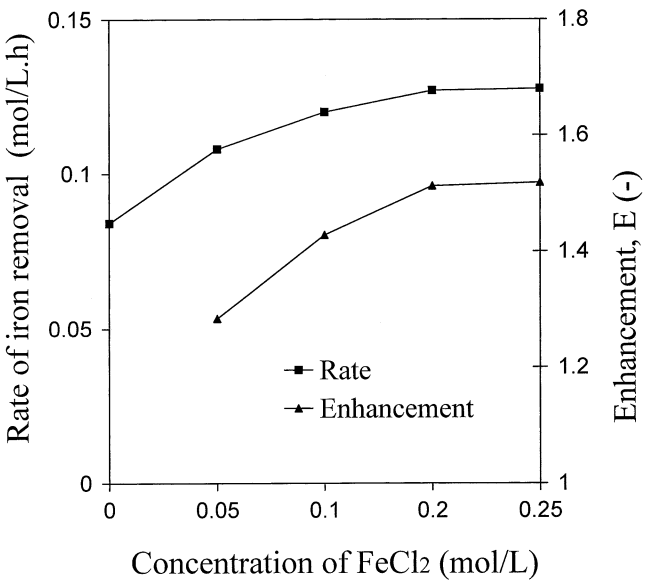

Fig. 1—Variation of rate of iron removal and enhancement in iron removal rate with concentration of ferrous chloride. Weight percentage of RI = 20. Particle size of RI = 210 to 250 μm.

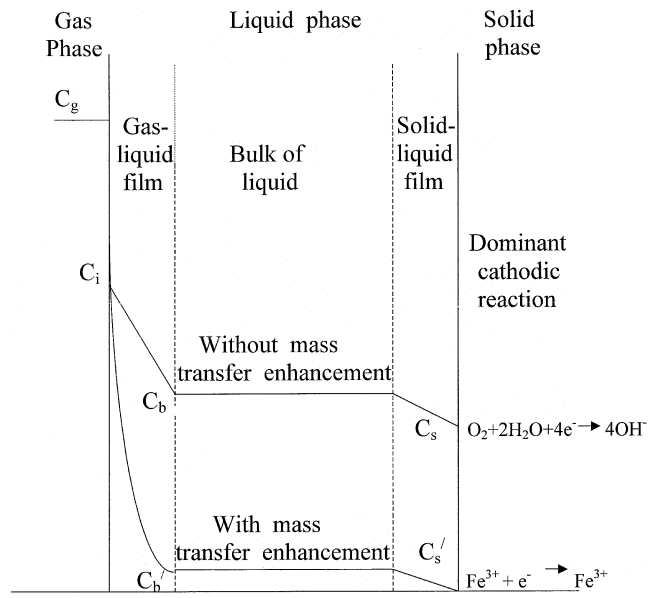

Fig. 2—Film model for gas-liquid mass-transfer enhancement.

Table I. Enhancement in Iron Removal Rate for Different Particle Sizes of RI* in Slurry

Range of particle size (μm)	Enhancement (E)
100 to 150	1.53
150 to 180	1.5
210 to 250	1.52

*Weight percentage in slurry = 20.

Table II. Enhancement in Iron Removal Rate for Different Weight Percentages of RI* in Slurry

Weight Percentage of RI	Enhancement (E)
10	1.49
20	1.52
30	1.5

*Particle size 210 to 250 μm.

thereby ensuring that the overall reaction involves the conversion of metallic iron to hydrated iron oxide only. The observed enhancement in the rate of iron removal due to the presence of ferrous chloride is interpreted by the theory of gas-liquid mass-transfer enhancement[8] in the following section.

Consider a gaseous component such as oxygen diffusing from the gas phase to a turbulent aqueous electrolyte solution. Since oxygen is sparingly soluble in aqueous solutions, the concentration gradient in the gas phase is negligibly small. According to the film theory,[9] the entire resistance to diffusion to the liquid lies in the stagnant liquid film of thickness δ_L, near the gas-liquid interface (Figure 2), where the concentration of oxygen varies from C_i at the interface to C_b in the bulk liquid. Then, the gas-liquid mass-transfer rate is given by

$$R_{gl} = \frac{D_0}{\delta_L}\left(C_i - C_b\right) \qquad [3]$$

where D_0 is the diffusivity of oxygen in liquid. The term D_0/δ_L is the gas-liquid mass-transfer coefficient and is expressed as k_L.

During the oxygen leaching process, oxygen transferred to the liquid phase reacts with ferrous ions according to the stoichiometric Eq. [2b]. The ferrous oxidation reaction is reported to be first order with respect to oxygen and ferrous ions in chloride solutions.[10] Hence, at constant pH, the rate equation for ferrous oxidation reaction in chloride solutions is

$$R_0 = k_0 C_0 C_{\mathrm{Fe}} \qquad [4]$$

where k_0 is the rate constant and C_0 and C_{Fe} are concentrations of oxygen and ferrous ion, respectively.

Depending upon the rate of this reaction, some amount of oxygen reacts within the film, while the rest is transferred across the film and reacts in the bulk of the liquid. If steady-state conditions are assumed in the film, material balances for the two reactants are

$$D_0(d^2C_0/dx^2) - k_0 C_0 C_{\mathrm{Fe}} = 0 \qquad [5]$$

$$D_{\mathrm{Fe}}(D^2C_{\mathrm{Fe}}/dx^2) - k_{\mathrm{Fe}} C_0 C_{\mathrm{Fe}} = 0 \qquad [6]$$

Based on the results of the solution of the preceding equations along with appropriate initial and boundary conditions, various reaction regimes have been discussed by Doraiswamy and Sharma.[8] The various reaction regimes are classified by use of the Hatta number:

$$\mathrm{Ha} = (D_0 k_0 C_{\mathrm{Fe},b})^{1/2}/k_L \qquad [7]$$

where $C_{\mathrm{Fe},b}$ is the concentration of the liquid phase reactant in the bulk liquid.

The slow and moderately fast reaction regimes are given by the following criteria: $0.02 < \mathrm{Ha} < 0.3$, slow reaction regime; and $0.3 < \mathrm{Ha} < 3$, moderately fast reaction regime.

In the slow reaction regime, a negligible proportion of

Table III. Computed Values of Hatta Number Corresponding to Various Fe^{2+} Concentrations

Concentration of Fe^{2+} C_{Fe} (mol/L)	Hatta Number (Ha)
1×10^{-3}	0.09
5×10^{-2}	0.6
0.10	0.9
0.20	1.27
0.25	1.42

oxygen reacts in the diffusion film. The process is essentially one of gas-liquid mass transfer followed by reaction in the bulk liquid. In the moderately fast reaction regime, the reaction is fast enough for a substantial amount of oxygen to react in the film rather than be transferred unreacted into the bulk liquid, resulting in a curved concentration profile, C_i C_b, as shown in Figure 2. The net result is gas-liquid mass-transfer enhancement.

Hatta numbers for various Fe^{2+} concentrations were computed using Eq. [7]. The influence of an electrolyte on the diffusivity of oxygen in aqueous solutions is reported to be dependent on the change in viscosity of the solution.[11] Since the change in viscosity of the $FeCl_2$ solution within the range of concentrations employed in the present study is negligible, D_0 was taken as the diffusivity of oxygen in water.[12] The value of k_0 was taken from a previous study.[7] Hatta numbers computed for various Fe^{2+} concentrations are listed in Table III. It shows that Fe^{2+} concentrations of 0.05 mol/L and above correspond to a moderately fast reaction regime. The Fe^{2+} concentration of 1×10^{-3} mol/L corresponds to a typical case where the reaction was started with NH_4Cl as the only electrolyte. A Hatta number corresponding to this concentration is in the slow reaction regime. According to the data reported by Charpentier,[13] the maximum gas-liquid mass transfer enhancement possible in the moderately fast reaction regime is around 1.5. Figure 1 makes it evident that the observed enhancements in the rate of iron removal for various concentrations of ferrous chloride are in the range of 1 to 1.5. This leads to the conclusion that the ferrous oxidation reaction is in the moderately fast reaction regime for the concentrations of ferrous chloride investigated in the present study.

Variation of particle size and weight percentage of reduced ilmenite in the slurry will lead to the variation of active surface area for solid-liquid mass transfer. However, since the process is controlled by gas-liquid mass transfer, enhancement is not affected by particle size and weight percentage of reduced ilmenite, as shown in Tables I and II.

When the Fe^{2+} oxidation is in the fast reaction regime, the liquid-phase concentration of oxygen will be negligible and hence oxygen will not be the dominant cathodic reactant at the surface of reduced ilmenite particles. In this case, Fe^{3+} ions could provide for the cathodic reaction as follows:[14]

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad [8]$$

Irrespective of the cathodic reactants, the rate of iron removal is proportional to the total amount of oxygen transferred to the liquid phase according to Eq. [1]. Hence, enhancement in the oxygen mass-transfer rate in the presence of ferrous chloride gives rise to an additional pathway for cathodic reaction through the presence of ferric ions.

Thus, it can be concluded that the intensification of the oxygen leaching process for iron removal can be achieved under environmentally acceptable conditions by the use of ferrous chloride as a mass-transfer enhancing agent. The mechanism of rate enhancement is interpreted by the theory of gas-liquid mass-transfer enhancement as due to the shifting of the gas-liquid mass transfer to a fast reaction regime leading to an additional cathodic reduction step involving ferric ions.

Since ferrous oxidation is an important reaction encountered with iron control in hydrometallurgy, the results of the present study will be useful to those involved in hydrometallurgical processes for iron control as well as for the process metallurgists involved in the manufacture of synthetic rutile. Interplay between mass transfer and kinetics reported in the present study will help in better interpretation of the results of the extensive studies on the kinetics of ferrous oxidation with dissolved oxygen.

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In-Situ Observation of TiN Precipitates at Stainless Steel/ CaO-Al_2O_3-MgO-SiO_2 Interface

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During the continuous casting of titanium-stabilized stainless and carbon steel grades, precipitation of TiN occurs

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